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Slow Precipitation and Dissolution of Solids Affects the Mobility of Heavy Metals in Soils

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What happens if soils are contaminated with heavy metals by agriculture, mining, or industry? Will the metals slowly leach into groundwater and pollute our drinking water resources? Will they be taken up by plants and finally end up in our diet? Environmental soil chemists are trying to answer these questions by determining the chemical forms, or species, of heavy metals in soils. Scientists at the Swiss Federal Institute of Technology in Zurich, Switzerland, have combined x-ray absorption fine-structure (XAFS) spectroscopy with a chromatographic soil column technique to determine the species and mobility of heavy metals in a typical, slightly acidic soil. Their results suggest that some metals (such as zinc) were relatively tightly bound by forming mineral precipitates, while others (such as cadmium) remain highly mobile.

Soil, or "dirt," as some people call it, is made up of an extremely complex mixture of minerals and natural organic substances. So, trying to understand how contaminants behave in such a complex environment might seem daunting, but soil chemists are currently making rapid progress by combining field observations and controlled laboratory experiments with modern spectroscopic techniques.

Our research team has combined two techniques, a chromatographic soil column technique and X-ray absorption fine structure spectroscopy (XAFS) to investigate the chemical behavior of zinc and other transition metals in a slightly acidic loamy soil, at realistically low metal concentrations.

Previous experiments have suggested that certain transition metals including cobalt, nickel and zinc can form structures called layered double hydroxide (LDH) when these metals

chemically react with clay minerals in neutral soils (neither acidic, nor basic) and relatively high metal concentrations. But these experiments have not shown clearly whether such structures can form in soils under more acidic conditions and at realistically low concentrations of metals from an infiltrating solution.

The objectives of our study were: (1) to investigate the rapid and slow absorption of cobalt, nickel, zinc and cadmium in a slightly acidic loamy soil; (2) to examine the subsequent release of metals

due to cation exchange and soil acidification; and (3) to assess the predominant absorption mechanisms of zinc in the soil.

One of the key techniques that we used is a chromatographic soil column technique. The basic idea is to pack a column with soil, and then leach it over a long time period with a solution containing small concentrations of cobalt, nickel, zinc and cadmium. When solid precipitates form slowly, the products accumulate over time in the soil column. At the end of this loading period, we can identify the precipitates and study how they re-dissolve by following changes in solution chemistry.

Solid precipitates of zinc were identified by using a technique called x-ray absorption fine-structure (XAFS) spectroscopy at beamline X11A of the National Synchrotron Light Source. In this technique, x-rays generated at the NSLS



Some of the Authors of the study (from left to right): Andreas C. Scheinost, Andreas Voegelin (lead author), Kurt Barmettler, and Ruben Kretzschmar.

are projected toward the precipitate, in which some of the photons of light are absorbed. By measuring the ratio of absorbed photons versus the total incident photons as a function of the energy of the incident photons, we can determine the nature of the chemical elements present in the precipitate.

Figure 1 shows three spectra, called radial structure functions, obtained by applying the XAFS technique to zinc-aluminum-LDH synthesized in the laboratory, soil from the column experiment after 41 days of loading, and the same

soil with zinc adsorbed in a geometry called inner-sphere surface complex (**Figure 1**, bottom right).

By analyzing the spectra, we suggest that a solid phase similar to zinc-aluminum-LDH has formed in the soil column. While zinc-aluminum-LDH and zinc-phylllosilicate (a phyllosilicate is a type of silicate mineral) cannot be distinguished easily based on the local structure, our leaching experiments demonstrate that the precipitates formed in the soil are readily re-dissolved upon acidification. Because zinc-phylllosilicates are expected to be

much less soluble, formation of zinc-aluminum-LDH seems most likely.

When different transition metals were compared, we found that the importance of precipitation of solid phases in the slightly acidic soil decreased in the order zinc-nickel-cobalt-cadmium, where zinc is the most tightly bound and cadmium is the most mobile. Our study has demonstrated that combining well-controlled laboratory studies with XAFS spectroscopy is a promising approach to investigate the behavior of metal contaminants in soils.

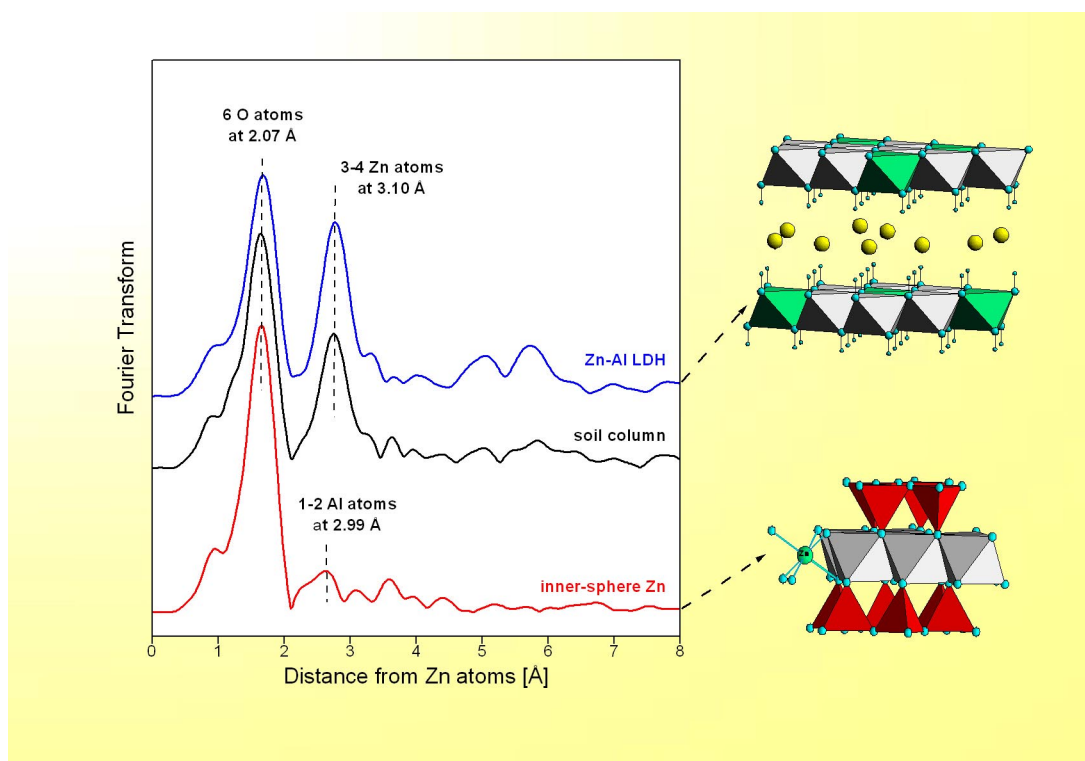


Figure 1. Identification of zinc species with x-ray absorption fine structure (XAFS) spectroscopy. After a slightly acidic soil column has reacted with a dilute zinc solution, zinc atoms are coordinated to six oxygen atoms at a distance of 2.07 angstroms (one angstrom is one tenth of a billionth of a meter), and to three or four zinc atoms at 3.10 angstroms. This local structure (middle curve) is similar to the solid phase zinc-aluminum-layered double hydroxide (Zn-Al-LDH), but is unlike the zinc inner-sphere surface complex. The structural drawings on the right side depict the two binding mechanisms (green: zinc octahedral; gray: aluminum octahedral; red: silicon tetrahedral; yellow: aqueous cations).